

A NOVEL APPROACH FOR THE ASSESSMENT OF THE RATE LIMITING STEP IN THE FISCHER-TROPSCH SLURRY PROCESS

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ABSTRACT

The rate limiting step in the Fischer-Tropsch (F-T) slurry process was assessed using a simple computer model. This model, unlike others, takes into account the water gas shift (WGS) reaction in the calculation of the importance of the gas-liquid mass transfer and makes use of the "Singular Kinetic Path" concept proposed by Espinoza in 1993. The predictions from the model showed that for the available catalysts the Fischer-Tropsch synthesis could be considered a kinetically-controlled process. CO has mass transfer coefficients lower than H_2 , is consumed by both F-T and WGS reactions, and is likely to be the limiting reactant in the process. The reactor performance could be improved by increasing the catalyst activity and operating in the mass-controlled regime. Also, an increase of the catalyst concentration up to a maximum of 37 - 40 wt.% could improve the reactor performance, although the reactor would be operating in a mass transfer-controlled regime due to the relatively high catalyst concentration.

INTRODUCTION

Numerous studies were dedicated to the improvement of the catalyst activity using reaction temperature for Fischer-Tropsch (F-T) synthesis and currently, a number of catalysts with high activity and better selectivity are available [5 - 7]. Several studies [12, 13] also pointed out that the kinetics of the reaction and the gas-liquid mass transfer were the only significant resistances in the slurry phase F-T process. These studies, however, failed to define whether such a process is kinetically- or mass transfer-controlled. In addition, these studies only focused on hydrogen and considered the F-T reaction expression without taking into account the Water Gas Shift (WGS) reaction. As a matter of fact, carbon monoxide is consumed by both F-T and WGS reactions and subsequently it could become a limiting reactant in the overall process.

Recently, a considerable attention has been given to the F-T synthesis in a slurry phase and several contributions covering the hydrodynamics, modeling, bubble size distribution and heat transfer have been published [1 - 4]. A detailed review on modeling of the F-T synthesis was carried out by Saxena et al. [6] and other models including complex ones such as that used in the scaleup of the Sasol I Slurry Bed Process (SSBP) [7] have been used. Most of these computer models were based on second order differential equations for both the gas and liquid phases as shown in Equation (1) for the gas phase and some include a solid mass balance to account for the catalyst concentration profiles which become an important variable when using low gas velocities.

$$D_g \epsilon_g \frac{d^2}{dz^2} (C_{g,i}) - \frac{d}{dz} (u_g C_{g,i}) - k_{L,i} a (C_{L,i}^* - C_{L,i}) = 0 \quad (1)$$

Other models such as that by Deckwer et al. [5] includes a heat balance in order to consider the temperature difference in the slurry reactor. These complex computer models include a large number of parameters concerning the hydrodynamics, kinetics, and mass as well as heat transfer. These parameters, however, are seldom available under the operating conditions of the F-T synthesis and the only resort is to estimate them using other literature data available for air/water systems, liquid hydrocarbons [8] or wax [3]. Unfortunately, the majority of these available data were obtained under atmospheric conditions which raises a serious doubt about their applicability under actual process conditions [9]. In addition, most of these data were obtained for gas-liquid systems without the presence of catalyst particles which alter the slurry density and viscosity as well as gas bubbles coalescence tendency. A thorough review concerning the effect of solid particles on mass transfer has been recently published by Beenackers and van Swaaij [10]. Other factors such as column internals are usually overseen despite the fact that their importance on the hydrodynamic behavior of the slurry reactor was reported to be significant [11]. Thus, using these complex computer models in order to predict the reactor performance as well as the rate limiting step in the F-T slurry process could be cumbersome, expensive, and the predictions are strongly dependent on the accuracy of the literature data used in these models.

This paper presents a novel approach to assess the rate-limiting step in the slurry phase F-T process. A simple computer model which takes into account the WGS reaction and uses the "singular Kinetic Path" concept proposed by Espinoza in 1993 is presented.

Development of the simple model

The two assumptions used in this model were: (1) the gas phase is a plug flow; and (2) the liquid phase is a series of CSTRs. Several simplifications were also made in: (1) phase mixing; (2) kinetics equation; and (3) calculation of mass transfer coefficients.

(1) Phase mixing:

The mixing in the liquid phase was simulated by a number of CSTRs arranged in series based on the studies of the "La Porte Pilot Plant" [14]. This eliminated the need for the second order differential term in the mass balance equations for the liquid phase. Also, the dispersion or backmixing in the liquid phase was expressed in terms of a series of CSTRs [15] as given in Equation (2).

$$\frac{1}{n} = \frac{2}{Pe} - \frac{2}{Pe^2} (1 - e^{-Pe}) \quad (2)$$

(2) Kinetic equation:

The use of various catalysts with different respective kinetic equations was overcome using the "Singular Kinetic Path" concept developed by Espinoza at Sasol [16]. His concept suggested that a single kinetic equation can be employed for any catalyst as long as the behavior of this catalyst resembles the shape of the F-T synthesis kinetic path when using iron catalyst. In the present model, the Anderson-Dry's equation given below (Equation (3)) was employed where the constant 3.5 was taken from Espinoza's work [16]. The Water Gas shift reaction rate was obtained by simplifying the one proposed by several authors [23,24].

$$r_{F-T} = A e^{\frac{E}{RT}} \frac{P_{H_2} P_{CO}}{P_{CO} + 3.5 P_{H_2O}} \quad (3)$$

$$r_{WGS} = k_{WGS} (P_{CO} - \frac{P_{H_2} P_{CO_2}}{K_{eq} P_{H_2O}}) \quad (4)$$

(3) Mass transfer parameters:

The correlation proposed by Akita and Yoshida [17] for aqueous systems is often used for predicting mass transfer coefficients in the F-T synthesis. In the present model, the correlation by Godbole et al. [8] for predicting mass transfer coefficients for oxygen in light hydrocarbon mixtures in a bubble column operating at a superficial gas velocity up to 0.2 m/s was used. This correlation is given by Equation (5).

$$k_{L,O_2} a = 0.31 U_g^{0.603} \quad (5)$$

The prediction of the mass transfer coefficients for hydrogen and carbon monoxide was carried out using the ratio of the diffusivities to the power (2/3) as in the Calderbank and Moo Young's correlation [18]. The presence of solids was also accounted for using the data presented in Figure 2 in the review by Beenackers and van Swaaij [10].

Determination of the rate limiting step using sensitivity analysis

Equation (6) was used to calculate the relative importance of the gas-liquid mass transfer resistance (α). This equation is similar to that presented by Deckwer et al. [5, 12], however, since the water gas shift activity of the catalyst is significant, it was incorporated in the equation through $\Phi(C_i)$ [19].

$$\alpha = \frac{\frac{1}{k_L a}}{\frac{1}{k_L a} + \frac{1}{K \Phi(C_i) \epsilon_L}} \quad (6)$$

$$\Phi_{H_2} = m V_T \epsilon_L (2A e^{-\frac{E_{FT}}{RT}} \frac{m_{H_2} C_{CO} R T m_{CO}}{C_{CO} m_{CO} + 3.5 C_{H_2O} m_{H_2O}} - B e^{-\frac{E}{RT}} (\frac{C_{CO}}{C_{H_2}} - \frac{C_{CO_2}}{C_{H_2O} K_{eq}})) \quad (7)$$

$$\Phi_{CO} = w V_T \epsilon_L (2A e^{-\frac{E_{FT}}{RT}} \frac{m_{H_2} C_{H_2} R T m_{CO}}{C_{CO} m_{CO} + 3.5 C_{H_2O} m_{H_2O}} + B e^{-\frac{E_{WGS}}{RT}} (1 - \frac{C_{CO_2} C_{H_2}}{C_{H_2O} C_{CO} K_{eq}})) \quad (8)$$

RESULTS AND DISCUSSION

Several scenarios including the Sasol I Slurry Bed Process (SSBP) were considered using the present simple model. Although the model did not consider the effect of pressure or temperature on mass transfer, the predictions from the model were comparable with those

predicted with a much more complex model used by Sasol [7]. To illustrate here the procedure, the operating conditions listed in Table 1 reported by Fox and Degen [19] were used. Different catalyst activities were also considered based on the work by Srivastava et al. [20].

The effects of the catalyst activity and concentration on the relative importance of gas-liquid mass transfer (α), relative liquid concentration ($C_{L,i}/C_{L,i}^*$), and $(CO + H_2)$ conversion were studied.

Figure 1 shows the effect of the catalyst activity on (α) and as can be seen hydrogen appears to differently behave than carbon monoxide, since the resistance to hydrogen reaches only 20% of the total resistance whereas that of carbon monoxide becomes significantly large. This difference can also be observed in the corresponding liquid concentrations. The sudden drop of the CO concentration with increasing catalyst activity could be attributed to the water gas shift reaction which also increases the H_2/CO ratio in the liquid phase. Based on this behavior, one can conclude that the reactor performance can be improved by enhancing the catalyst activity although the reactor can be operating in a mass transfer-controlled regime. It should be mentioned, however, that the improvement of the reactor performance from 0.41 to 0.44 $kg(HC)/kg(Fe)/hr$ would require an increase of about 60% in the intrinsic catalyst activity.

The effects of catalyst concentration on (α) as well as the $(CO + H_2)$ conversion is illustrated in Figure 3 and as can be noticed the hydrogen and carbon monoxide resistances appear to increase with increasing catalyst concentration. Also, the increase of catalyst concentration almost produces a proportional improvement of $(CO + H_2)$ conversion, particularly, at low levels. The effect of high solid loading on the mass transfer rate, however, drove the process into a mass transfer-controlled regime and subsequently, the $(CO + H_2)$ conversion appeared to decrease. The maximum conversion could be achieved with a catalyst concentration between 35 and 40 wt%. Thus, the other approach to increase the reactor performance is by increasing the catalyst concentration and subsequently the catalyst becomes slightly under utilized and the mass transfer becomes the controlling rate. Nevertheless, one drawback of this approach is that at high catalyst concentrations, the separation of the catalyst from the wax becomes a critical step in the synthesis process. According to our knowledge, only two companies have successfully solved this separation step: Sasol and Exxon with their iron and cobalt catalysts, respectively.

CONCLUDING REMARKS

Based on the operating conditions and catalysts used in the simple model developed in this study, the following concluding remarks can be made:

1. The slurry phase Fischer-Tropsch synthesis with the present catalysts can be considered a kinetically-controlled process and it would require a substantial improvement of the catalyst intrinsic activity in order to change this situation.
2. The slurry reactor performance for F-T synthesis can be improved by increasing the catalyst activity and/or catalyst concentration, although, the increase of catalyst concentration up to 40 wt%, will drive the process into a mass transfer controlled-regime.
3. Since CO has a lower mass transfer coefficients than those of H_2 [22] and is consumed by Fischer-Tropsch and water gas shift reactions, it is likely to be the limiting reactant.
4. The mass transfer coefficients for H_2 and CO were predicted in this study and therefore they should be measured under the actual Fischer-Tropsch operating conditions in the presence of typical catalyst concentrations. Experimental data are also needed in the presence of high catalyst loading.

Nomenclature

| | |
|----------|---|
| A | Fischer Tropsch intrinsic catalyst activity, kmol of C to HC/kg.Fe.bar.s |
| B | Water Gas Shift intrinsic catalyst activity, kmol of C to HC/kg.Fe.bar.s |
| a | gas-liquid interfacial area relative to the expanded fluid volume, m^{-1} |
| C | concentration, $kmol/m^3$ |
| C* | Concentration at saturation, $kmol/m^3$ |
| D | Dispersion coefficient, m^2/s |
| E | Apparent activation energy, J/mol |
| K | Overall kinetic constant, s^{-1} |
| k_{eq} | Water gas shift equilibrium constant, $k_p = \exp(4577.8/T-4.33)$ |
| k | mass transfer coefficient, m/s |
| m | solubility |
| n | number of CSTRs in series |
| Pe | Peclet number, $u_s L/\epsilon_s D_s$ |
| P | Partial pressure, bar |
| R | Gas constant, J/mol.K |

| | |
|----------------------|---|
| u | velocity, m/s |
| V_T | Fluidized bed volume m^3 |
| w | catalyst concentration (kg/m^3) |
| z | axial position, m |
| <u>Subscript</u> | |
| i | component i |
| g | gas phase |
| L | liquid phase |
| <u>Greek symbols</u> | |
| ϵ | holdup |
| α | relative extent of the mass transfer resistance |

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TABLE 1

Fischer Tropsch slurry bed design basis: From Fox and Degen [19]

| | | |
|----------------------|------|----------------|
| Diameter | 4.8 | m |
| Length | 12.0 | m |
| Cross Sectional Area | 15.2 | m ² |
| Reactor Volume | 211 | m ³ |
| Temperature | 257 | °C |
| Pressure | 28.3 | atm |
| Slurry Concentration | 35.0 | wt. % |
| Gas Velocity | 0.14 | m/s |
| Catalyst Performance | 0.41 | Kg/Kg.hr |

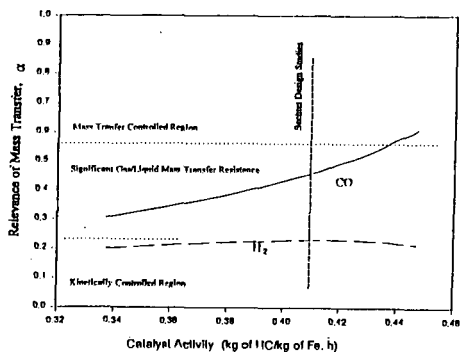


Figure 1: Effect of catalyst activity on the relative mass transfer resistance (α).

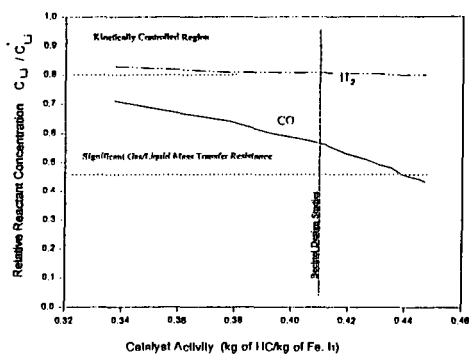


Figure 2: Effect of catalyst activity on the reactants liquid concentration.

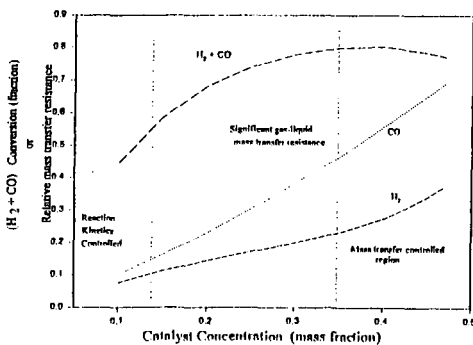


Figure 3. Effect of catalyst concentration on H₂+CO conversion and on the relative mass transfer resistance (α).